Supporting Information

The impact of grafted surface defects and their controlled removal on supramolecular self-assembly

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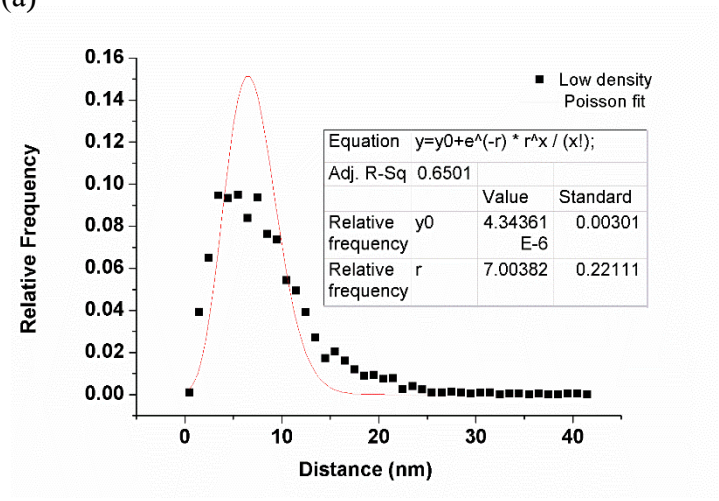
Section S1. Description of data processing

A statistical analysis on the nearest neighbor distance of grafted pins and the average domain size ISA-OC18 assemblies were performed using SPIP® software (Image Metrology). Determining the fractal dimensions of ISA-OC18 domains and the linear density of pins located at the domain borders were done using WSxM software [1]. For each regime- bare HOPG, low (20^0C/25^0C) and high density grafting- 200 nm × 200 nm individual STM images (different areas and, when necessary, different sessions) were used to collect and analyze 120-140 complete well-defined domains. In the case of the experiments involving annealing to elevated temperatures (60^0C), incomplete domains were also counted since we were primarily interested in determining the size and population of the smallest domains that remain after annealing. Images from the same selection were also used for the analyses of pin placements and fractal dimensions of self-assembled domains. Unless otherwise noted, a bin size of 1 nm and 400 nm^2 were chosen for the nearest neighbor distance and average domain size distribution determination, respectively.

Section S2. Analysis of the randomness of pin placement

- Analysis of grouped images

(a)



(b)

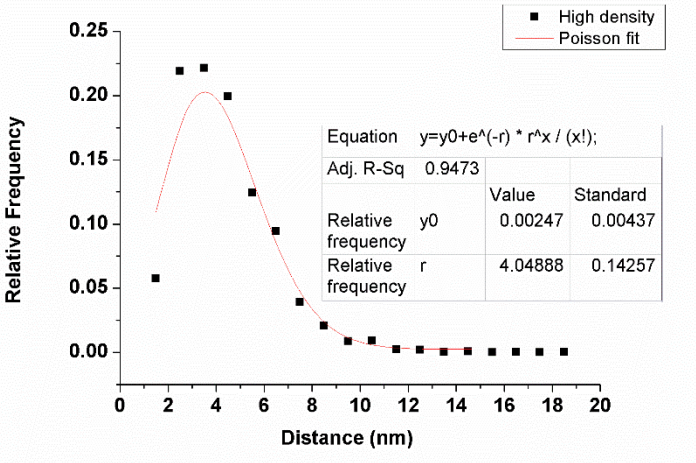
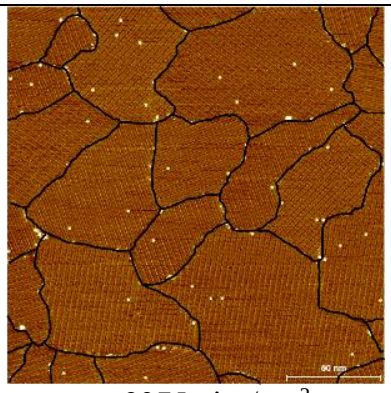
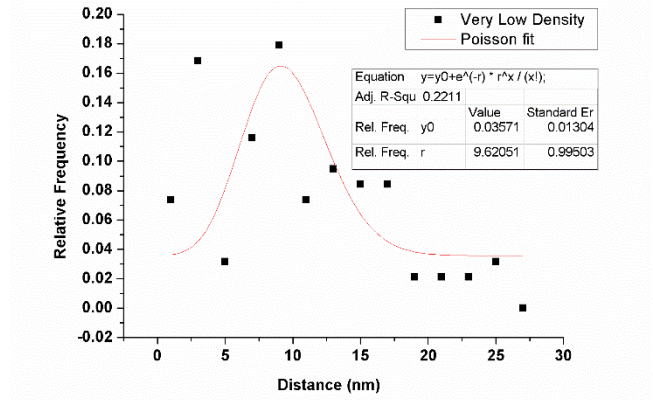
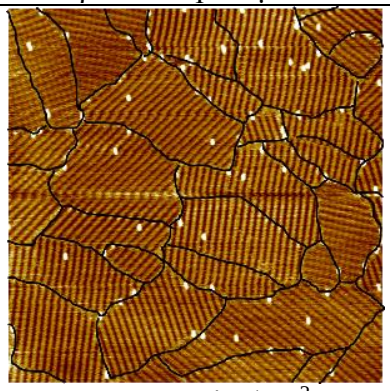
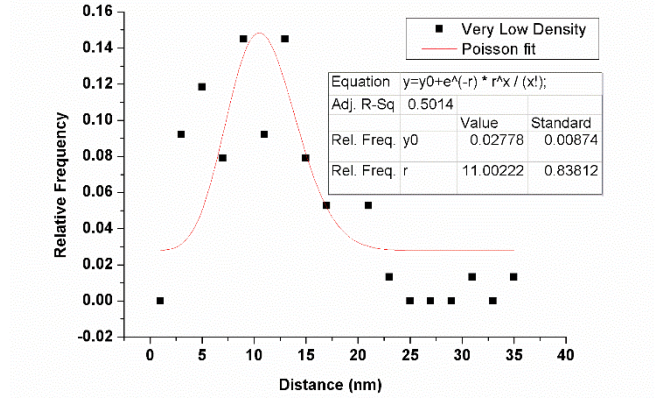
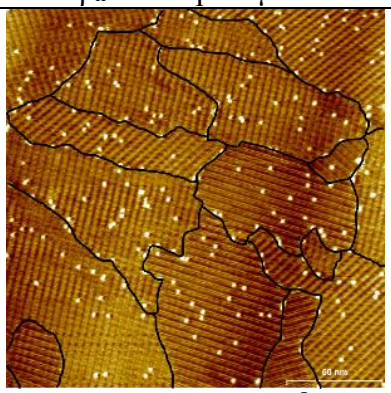
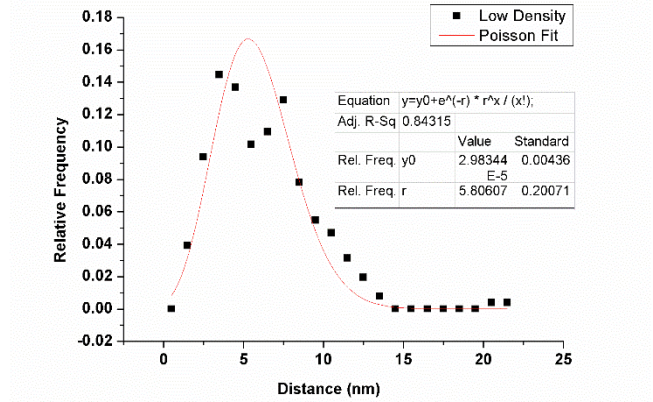
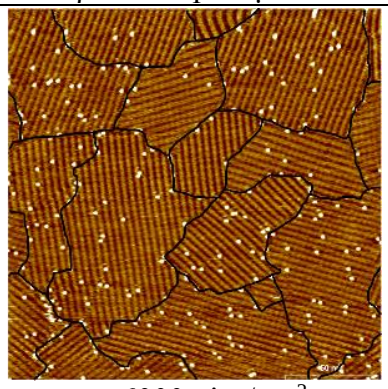
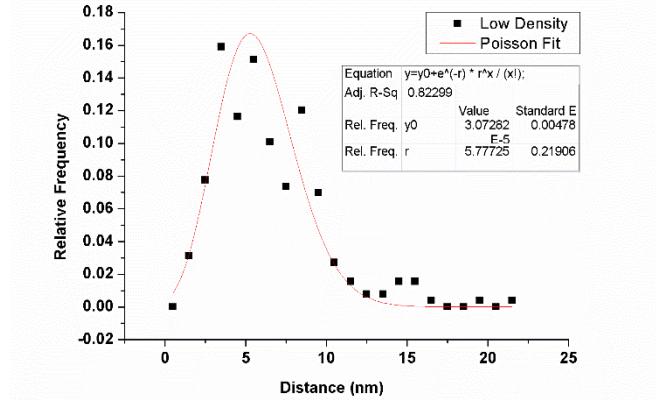


Figure S1 – Histogram revealing the distributions of the nearest-neighbour distances of pins on HOPG in a set of STM images with a) low - (ρ_n=1500-6000 pins/μm^2) and b) high-density (ρ_n=13000-22000 pins/μm^2) grafting. A Poisson fit is superimposed in each case.

- Analysis of individual images

Very Low Grafting Density *	 ρ_n=2375 pins/μm^2	
	 ρ_n=1900 pins/μm^2	
Low Grafting Density	 ρ_n=6000 pins/μm^2	
	 ρ_n=6000 pins/μm^2	

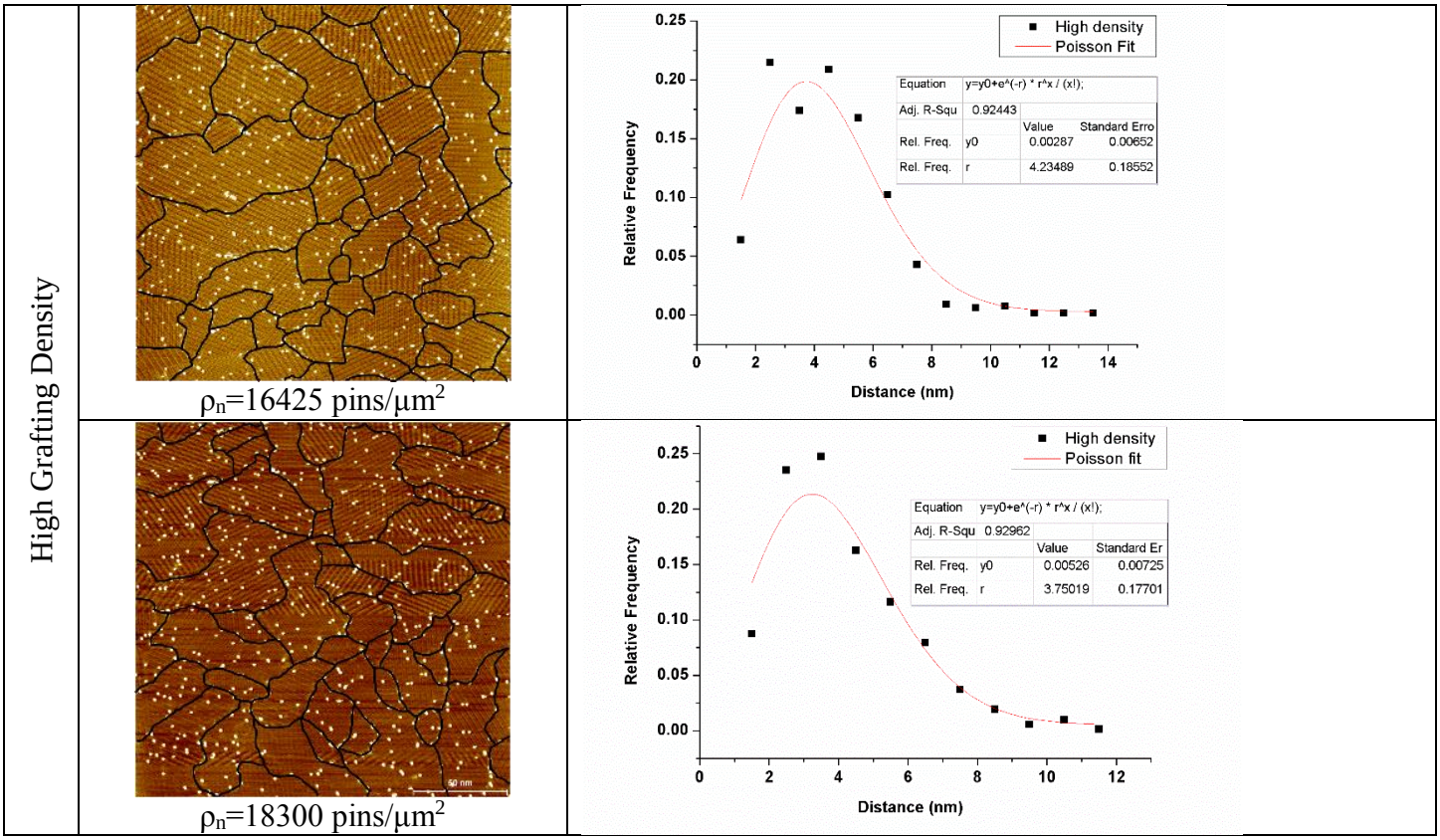


Table S1. Distribution of the nearest-neighbour distances of pins from two representative images for each grafting regime. A Poisson fit is superimposed in each case.*(* bin size=2nm)*

The analysis of pin placement was performed for individual STM images and for sets of images with different grafting densities. Except for the images with very low grafting density (<4250 pins/μm^2, i.e. less than 170 pins per image) in which there were no clear trend, other images have shown asymmetric grouping of pins that with varying accuracy (better for the larger datasets- i.e. individual images of the samples with high grafting density and analyses of groups of images) can be fitted to Poisson distribution. We believe that a separate detailed investigation is necessary to reliably confirm/rule out minute details in the pin distribution (like somewhat excessive clustering in the case of the samples with high density of pins). Thus, for simplicity throughout this paper we will refer to our samples as being grafted randomly.

Section S3. A note added in response to a reviewer comment.

A reviewer's comment:

In the discussion of the high defect density samples with self-assembly carried out at 20°C the authors state: 'The increased number of pins, as well as the lowered distance between them (Fig. 2E) in the samples with high grafting density, makes arrays of pins to act as barriers slowing down the domain growth. Consequently, new crystals nucleate on yet uncovered substrate, eventually yielding a monolayer composed of many small domains.'

This is a reasonable hypothesis but how can the authors be sure that the defects do not themselves act as nucleation sites? An increase in the nucleation rate associated with additional nucleation sites, rather than a slowing down of the rate of domain growth, would have a similar effect on the distribution of domain sizes.

Author reply:

First of all, we would like to point out once again that "low" and "high" grafting densities are the results of arbitrary grouping: samples that did not significantly skew the domain size distribution at the specific experiments performed at 20°C were named to have "low" grafting density, those that did alter the domain size distribution were assigned to have "high" grafting density. Thus, the same experiments performed at 25°C have shown that "low" density is quite effective at influencing self-assembly.

If the pins indeed promoted nucleation than every pin on the surface would increase probability for an extra nucleation and monotonous rather than stepwise change in the domain size distribution should be expected. The observed "inactivity" of pins until certain critical density (specific for the exact self-assembly conditions) is indicative that not nucleation but growth and/or ripening steps of 2D crystal growth are being affected by grafted sites. Since at 20-25°C ripening of ISA-OC18 is very slow we concluded that pins alter the growth of nucleated 2D crystals and proposed a possible mechanism.

Section S4. Influence of temperature (20°C vs. 25°C) on domain sizes in the low density grafting regime

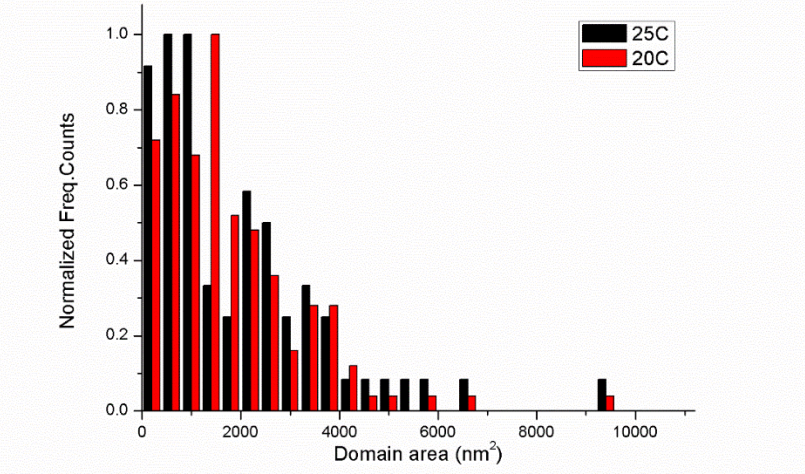


Figure S2. Histogram revealing the domain size distribution of ISA-O-C18 assembled at 20^{0}C and 25^{0}C on modified HOPG with a low density of grafted species.

Section S5. Influence of annealing to 60°C on domain sizes in the high density grafting regime

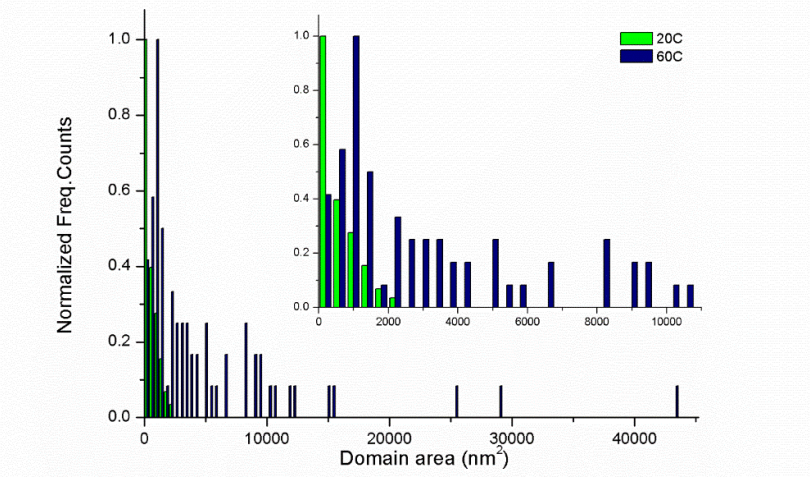
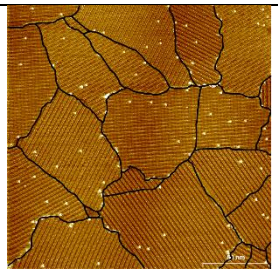
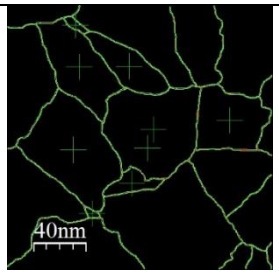
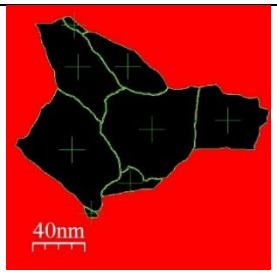
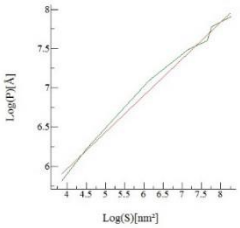
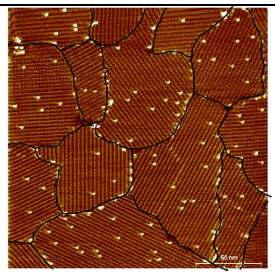
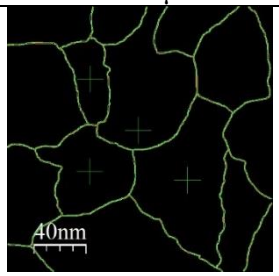
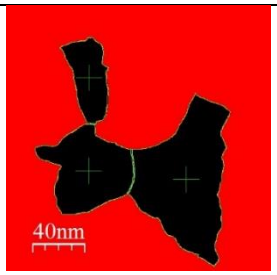
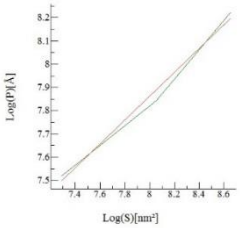
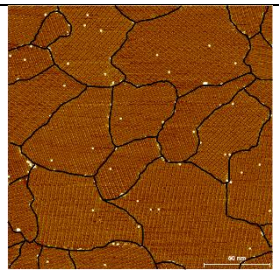
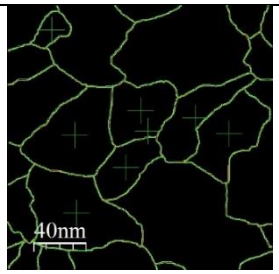
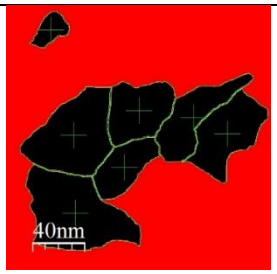
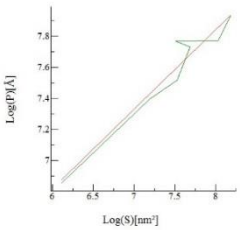
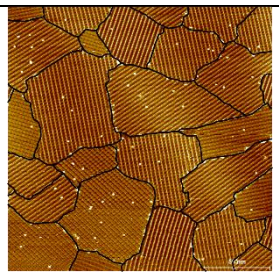
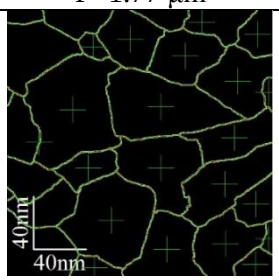
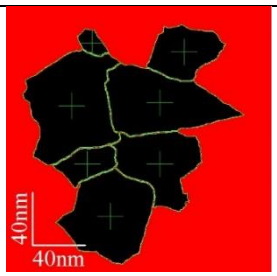
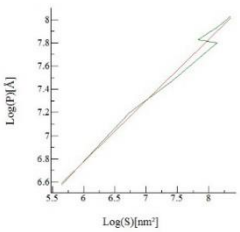
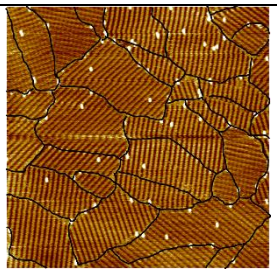
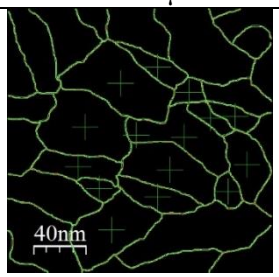
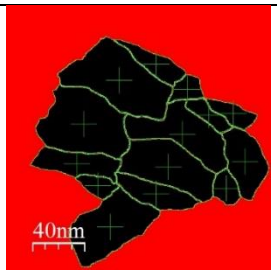
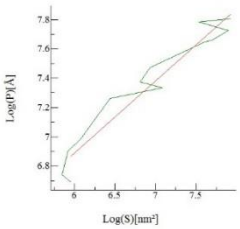
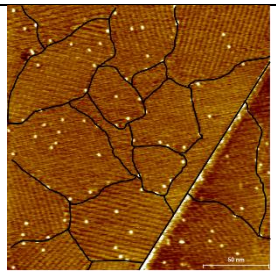
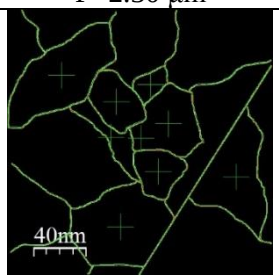
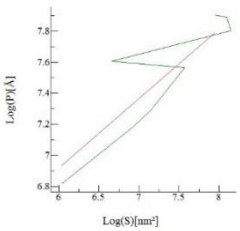
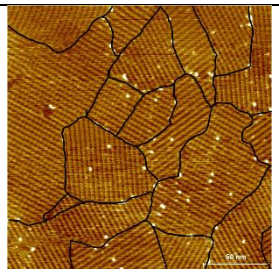
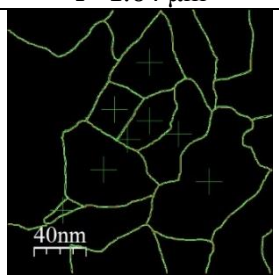
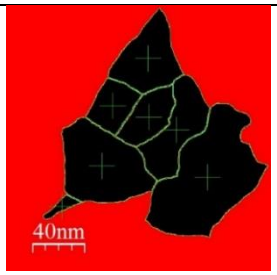
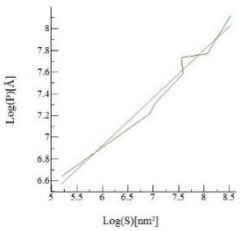
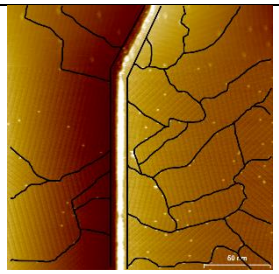
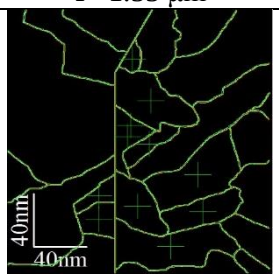
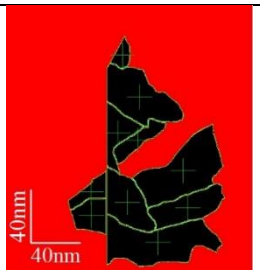
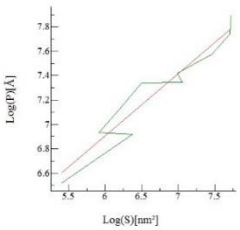


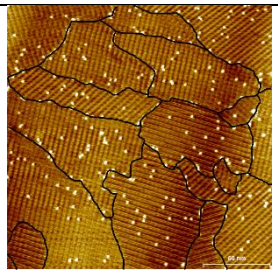
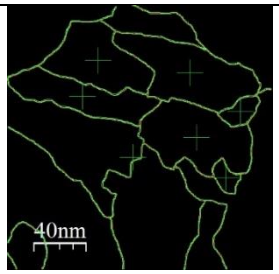
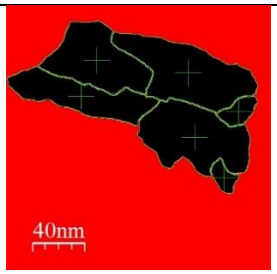
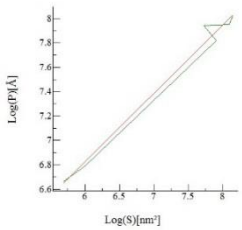
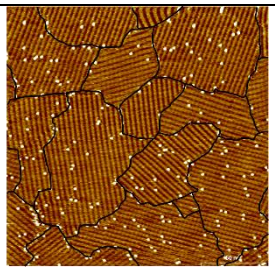
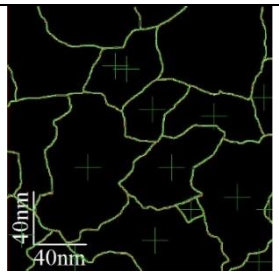
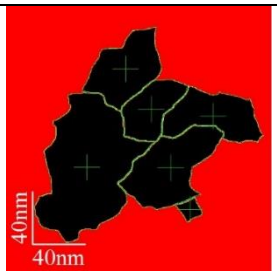
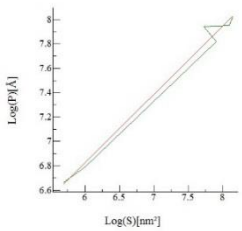
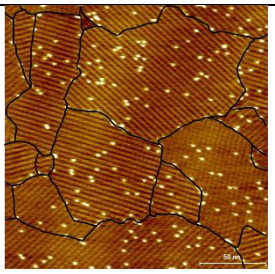
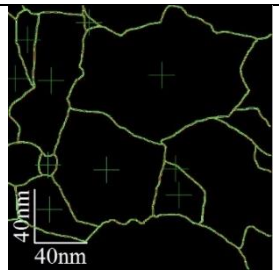
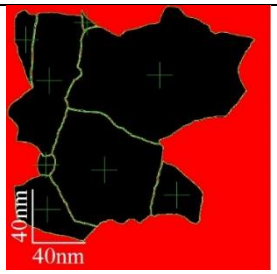
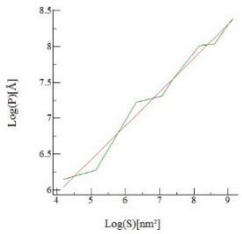
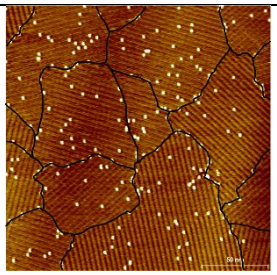
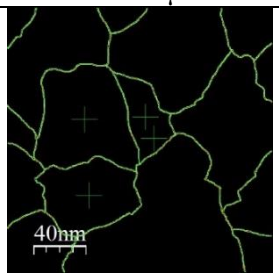
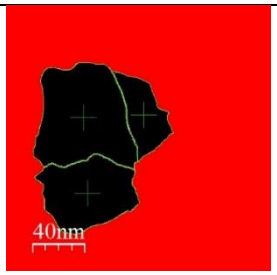
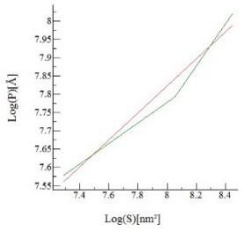
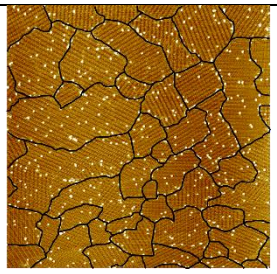
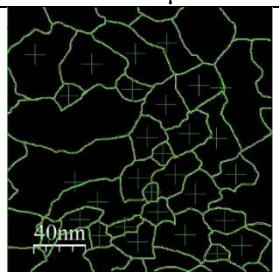
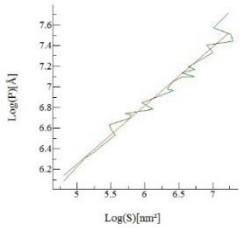
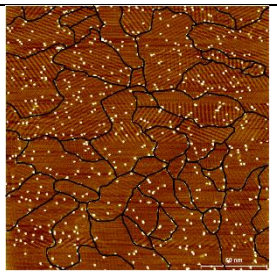
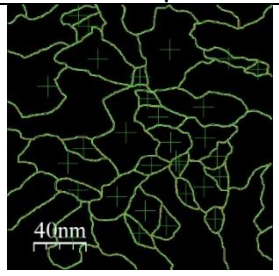
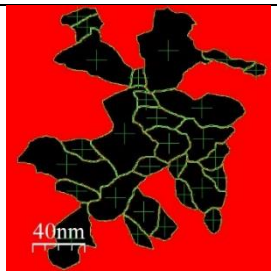
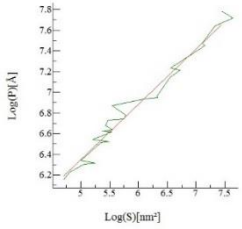
Figure S3. Histogram revealing the domain size distribution of ISA-O-C18 (0.2mM) assembled at 20^0C with and without sequential annealing (5 mins at 60^0C) on modified HOPG with a high density of grafted species.

Section S6. Linear pin densities at the domain boundaries and fractal dimensions of ISA-OC18 domains

By performing a fractal analysis, it is possible to obtain information about the auto similarity of the shapes of different objects in an image. The slope of the fit line (fractal dimension) of the plot Log(Perimeter) versus Log(Area), gives the power of the area related to the perimeter. For further information, see help file from WSxM Software. [1]

	# [a]	# pins at boundary (# pin / boundary length) [b]	Original image [c]	Total perimeter [d]	Fractal analysis image [e]	Fractal dimension [f]
Low density, 20^0C	#1	61 (40%) (42 defects/µm)		 P=1.58µm		 D=0.93341
	#2 **Fig 4A**	72 (49%) (52 defects/µm)		 P=1.38µm		 D=1.02483

	#3	65 (71%) (37 defects/µm)		 P=1.77 µm		 D=1.02015
	#4	58 (50%) (31 defects/µm)		 P=1.87 µm		 D=1.05002
Low density, 25°C	**#1 Fig 5B**	53 (71%) (23 defects/µm) *(very low grafting density)*		 P=2.30 µm		 D=0.98228
	#2	49 (52%) (30 defects/µm) *(very low grafting density)*		 P=1.64 µm		 D=0.89169
	#3	37 (59%) (24 defects/µm) *(very lo w grafting density)*		 P=1.55 µm		 D=0.87989
	#4	104 (78%) (54 defects/µm) *(very lo w grafting density)*		 P=1.93 µm		 D=1.01822

	#5	106 (42%) (68 defects/µm) *(low grafting density)*		 P=1.55 µm		 D=1.12348
	#6	110 (46%) (69 defects/µm) *(low grafting density)*		 P=1.59 µm		 D=1.07089
	#7	84 (39%) (56 defects/µm) *(low grafting density)*		 P=1.49 µm		 D=0.94564
	#8	86 (40%) (67 defects/µm) *(low grafting density)*		 P=1.28 µm		 D=0.73749
High density, 20°C	**#1 Fig 4B**	314 (48%) (109 defects/µm)		 P=2.89µm		 D=1.13580
	#2	343 (47%) (120 defects/µm)		 P=2.86 µm		 D=1.07272

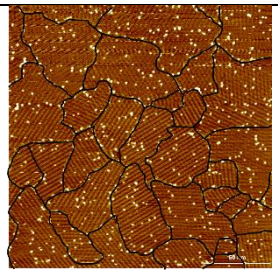
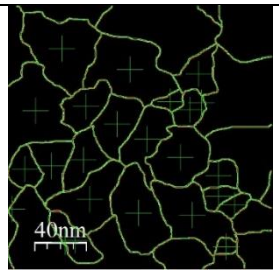
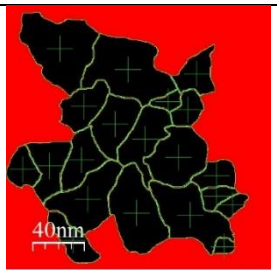
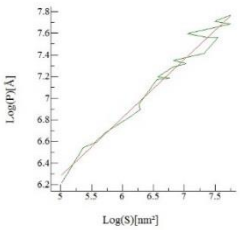
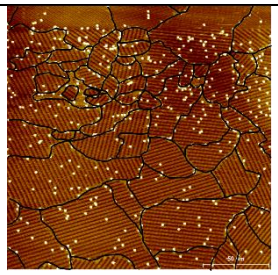
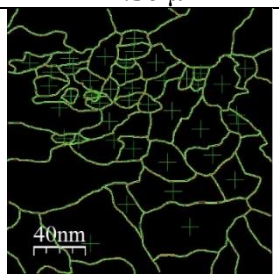
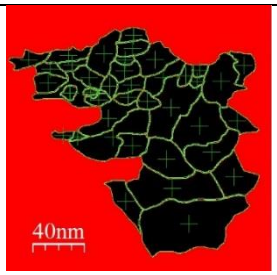
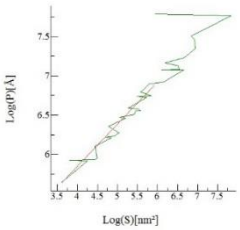
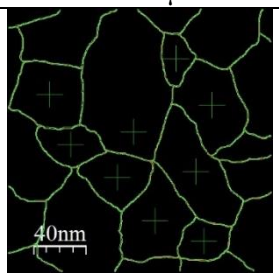
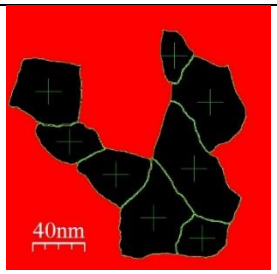
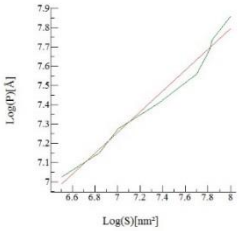
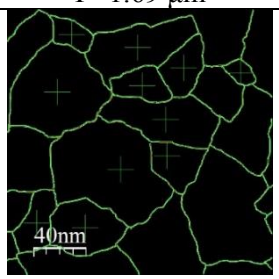
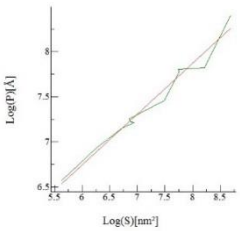
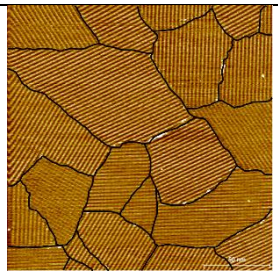
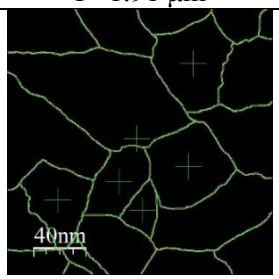
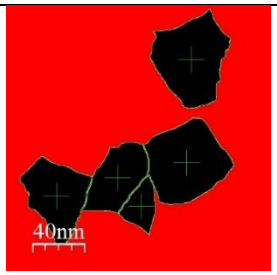
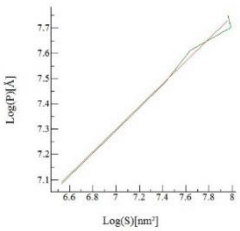
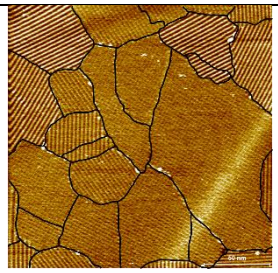
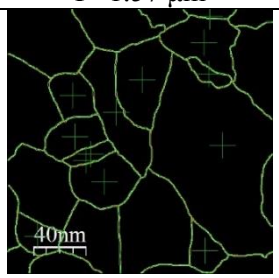
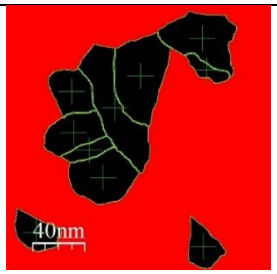
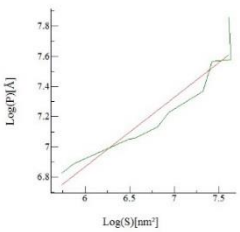
	#3	268(40%) (117 defects/μm)		 P=2.30 μm		 D=1.07571
	#4	377(69%) (124 defects/μm)		 P=3.05 μm		 D=1.06826
Bare HOPG	**#1**			 P=1.69 μm		 D=1.08282
	#2			 P=1.91 μm		 D=1.12971
	#3			 P=1.57 μm		 D=0.89591
	#4			 P=1.76 μm		 D=0.92271

Table S2. Additional analysis on four representative images of each regime (low grafting density at 20^0C and 25^0C, high grafting density at 20^0C and bare HOPG) , including: a) sample identification, b) number (and relative percentage) of pins located within the domain boundary; ratio between the number of pins per unit length of domain boundary, c) original STM image with highlighted domain boundaries , d) total perimeter length selection, e) (complete) domains selected for fractal analysis, f) fractal dimension determination using WSxM software [1].

Based on this analysis we do not see an appreciable difference in the complexity of domain borders of ISA-OC18 assemblies on pristine HOPG, samples with "low" and "high" grafting densities. Introduction of pins changes the size of the domains and not the complexity of their shape. Also, the linear density of pins located at domain borders naturally increases with the increase of the grafting density while the ratio between pins at the border and those located inside domains varies within the same broad range (~45-70%) irrespective of grafting density.

Section S7. Directed ripening of domains *via* tip-assisted removal of grafted pins

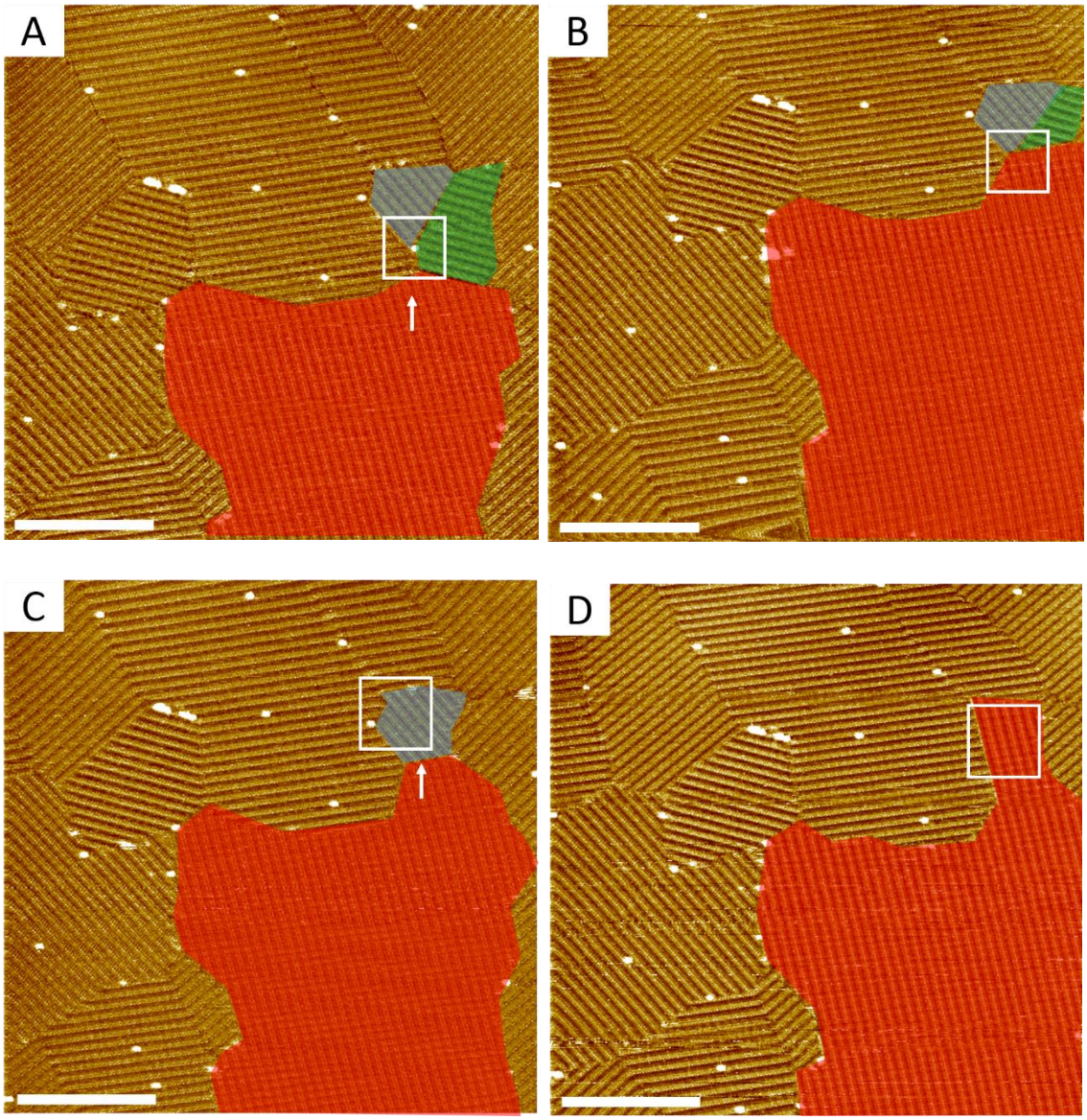


Figure S4. STM images of ISA-OC18 (0.2 mM) on modified HOPG with a low density of grafted species where pins enclosed within the marked areas (white squares) a) and c) were locally removed using mild STM lithography conditions (V_s = -0.001 V, I_t = 200 pA). Ostwald ripening followed in the degrafted zones b) and d) in the next scan (V_s = -0.720 V, I_t = 70 pA, scale bar = 40 nm).

References

[1] I. Horcas, R. Fernandez, J.M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero and A. M. Baro, Rev. Sci. Instrum. 78, 013705 (2007)